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**INTERDISCIPLINARY RESEARCH CONCERNING
THE NATURE AND PROPERTIES OF CERAMIC MATERIALS**

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CONCERNING THE NATURE AND PROPERTIES OF
CERAMIC MATERIALS Semiannual Status Report
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Semi-Annual Status Report Number 25

December 30, 1975



**University of Washington
College of Engineering**

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INTRODUCTION

This report describes research upon the nature and properties of ceramic materials being undertaken by and under the supervision of faculty members of the University of Washington. The research is of an interdisciplinary nature and the direct result of support by NASA grant NGL 48-002-004. The University recognizes the need for educational and basic research programs on materials and proposes to continue support of this and other appropriate programs within available resources.

In the early 1960's, government sponsorship of interdisciplinary research upon materials at various U.S. institutions was in its early stages. The National Aeronautics and Space Administration determined the need to establish a similar program restricted to ceramic materials, since the bulk of the research in the IDL efforts then in effect was related to solid state physics and physical metallurgy. The award of the grant to this institution in 1963 and the subsequent supplements have resulted in a unique research program with a pre-planned narrow scope.

Upon receipt of the initial grant, a research committee and an administrative board were established for the operation of the program. During the past year the functions of the two committees were combined into a single unit, the membership of which is given in Appendix I.

PROGRAM GOALS

The goals of the Ceramic Materials Research Program are:

1. Accomplish significant fundamental research on the nature and properties of ceramic materials relevant to this country's needs, particularly those of interest to NASA.
2. Develop a center of excellence for ceramic research at this institution.
3. Further interdisciplinary research by encouraging colleagues in other disciplines to relate their research interests and techniques to ceramic materials.
4. Provide an opportunity for highly qualified students to continue their educational objectives in materials science and engineering, particularly in ceramic engineering.

5. Develop a procedure for improving communication between academic, governmental and industrial people having common interests in ceramic materials.

It is our contention that interdisciplinary research involves individuals from different, recognized disciplines contributing their knowledge and expertise to a common, well-defined problem. This is no simple task, especially when designing a program involving the complexities of ceramic materials. We have therefore attempted to define those types of fundamental problems which are relevant and most appropriate to university research, then couple individuals from other science and engineering disciplines with the faculty in ceramic engineering to attempt a solution. These are the means by which we are attempting to attain the third goal. Assessment of progress is difficult, but we have been and will continue to develop and test appropriate techniques for the improvement of our interdisciplinary research.

We believe that progress towards the first three goals can best be obtained through continued communication, not only between ourselves but with others having common research interests and knowledge outside the University. Geographic isolation and distance offer an obstacle unique to this area, but the availability of funds for travel has reduced this to some degree.

PROGRAM OBJECTIVES

The following objectives were established for 1975-76.

1. Continue visitations and contacts with NASA research centers and other government facilities to obtain firsthand knowledge of future ceramic material requirements.
2. Assessment of program to determine the total relevance of our efforts to future material requirements of various agencies.
3. Orientation of program as dictated by 1 and 2 above.
4. Integrate research funded from other sources.
5. Increase research efforts from other sources.

Progress towards attainment of these was as follows.

1. Visits during the current report period were made to Lewis and Ames. We would have liked to have had a representation at the OAST advanced planning meeting in November, but notification was not received until after the meeting.
2. Several meetings of the Research Committee have been held to evaluate the current program with respect to relevance. It was determined that, with minor changes, the program can contribute to future ceramic materials requirements. Further evaluation will continue as additional information becomes available regarding NASA's future planning.
3. No major reorientation of the program is planned at present.
4. Continuing research supported by several sources of additional outside funding have been integrated into the program as will be reported in the research section.
5. Limited funding has precluded any major expansion of this with grant funds, however outside support has been obtained from NASA-Ames and from the U.S. Navy.

USE OF CMR FACILITIES

A major contribution of grant funds in past years has been the purchase of capital equipment. Although this was originally obtained in direct support of the CMR program, its availability has aided in other University research. A list of some of the users of this equipment during 1974-75 was given in the last status report. Another compilation will be presented in the year-end report to be submitted in June.

RESEARCH PROGRAM

When the research was originally established through award of the grant in 1963, it was planned to study the effects of various energy environments upon ceramic materials. As stated earlier, we have consistently identified rather specific research areas as a means of improving the interdisciplinary flavor. Interests of the faculty and relevance have necessitated modifications to these identifiable research areas over the past years.

A major reorientation has taken place over the past three years. The research on optical degradation and on refractory structural ceramics has been terminated. In both cases, research continued until support

commitments were completed under the step-funding conditions of the NASA grant. The research upon the mechanisms of fast-ion transport was begun in 1973 and the new research area on ceramic fibers was initiated during the past year.

In this report, each of the research areas will be considered as a separate entity, since each is a basic unit of our interdisciplinary efforts.

SOLID ELECTROLYTE RESEARCH AREA
Professor Suren Sarian, Area Coordinator

Relevance:

There is a continuing requirement for high power-density batteries for space and earth-bound vehicles. Development of these has been hindered by the lack of a totally satisfactory solid electrolyte. This research is directed towards obtaining basic knowledge appropriate to this problem.

Goals:

1. To increase the knowledge of the mechanism of ionic transport in solids.
2. To develop a model for synthesis of effective ionic conducting materials for high power-density batteries.

The basic problem is an understanding of the mechanism of ionic transport in single crystal and polycrystalline ceramics. Knowledge of ion mobility in solids could have significance in obtaining basic information regarding high temperature solid reactions in ceramics as well as in the studies related to solid electrolytes.

The Kinetics and Mechanisms of Ultra-Fast Ion Transport in Solid Electrolytes

Faculty Supervisor: Suren Sarian, Research Associate Professor
Ceramic Engineering

Graduate Assistants: Bonnie J. Dunbar, M.S. Candidate
Research Assistant

William J. McEntee, M.S. Candidate
Research Assistant

David Brooks, M.S. Candidate
Research Assistant

Brian Seegmiller, M.S. Candidate

Purpose: To study the kinetics and mechanisms of very rapid ion transport in solid electrolytes:

1. isotope mass effect diffusion experiments in single crystal and hot-pressed polycrystalline for beta-alumina; and
2. measure the effect(s) of microstructural features and H₂O on the mass transport rate.
3. determine the Haven ratio, and isotopic mass effect in single crystal RbAg₄I₅.
4. measure the Na⁺ exchange rate between single crystal beta-alumina and a suitable organic electrolyte.

Relevance:

A number of ionic solids exhibit an ambient temperature electrical conductivity which is often as high as the conductivity of many concentrated aqueous electrolytes. These solid electrolytes are potentially useful as high energy and power density re-chargeable batteries. Determining, unambiguously, the atomistic mechanism(s) of ultra-fast ion transport in known ambient temperature conducting solid electrolytes will isolate many of the factors which make low temperature ionic conductivity possible in certain compounds but not in others and aid in the search for additional ionic conducting compounds.

Objectives:

Diffusion correlation effects, arising from non-random successive atomic displacements will be determined by isotopic mass effect and the Haven

ratio. These studies will be conducted with single crystal sodium beta-aluminas and single crystal RbAg_4I_5 and will be coupled to the results of NMR and conductivity measurements, to give information concerning the mechanisms of very rapid ionic transport in solid electrolytes. These studies have been completed for beta-alumina and will be continued using RbAg_4I_5 .

While RbAg_4I_5 is not a suitable candidate for use in high power density systems, it serves as an important vehicle for research studies because it has the highest ionic conductivity of any known solid. The non-conducting ions form a relatively rigid cubic lattice containing a very large number (54) of sites through which the electroactive silver ions diffuse. However, the diffusion mechanism, as well as the type and number of active sites, remains unclear. Tracer diffusion measurements have been made in polycrystalline RbAg_4I_5 , but these data are unreliable since it is well known that grain boundaries have a profound effect on the ion transport kinetics. Conductivity measurements have been made on single crystal material. Therefore, the tracer diffusion coefficients will be measured using high quality single crystals; $^{105}\text{Ag}/^{111}\text{Ag}$ isotope effect will also be studied. These data will give the Haven ratio, and the correlation factor for diffusion, and, thus, provide clues as to the diffusion mechanism(s). This work, coupled with the EXAFS studies being conducted by Professor Stern, will also aid in determining which of the three types of sites are active in the conduction process. This work will be completed by September 1976.

The effect of microstructural features on the mass transport rate are being studied using polycrystalline sodium beta-aluminas having varied preferred orientation. The effect of water, as a blocking impurity, has also been examined. This work will be completed by June 1976.

Organic electrolytes in Na/S and N/halogen cells are receiving growing interest. Organic solvents, when used in conjunction with beta-alumina, are attractive as separators (i.e., allow passage of the electroactive sodium ions but prevent S_x ions or corrosive halogens from contacting the anode), permit lower operating temperatures (i.e., operation of the cell at $\approx 150^\circ\text{C}$ rather than the 300°C now required with molten S), and eliminate wettability problems (i.e., liquid organic solvents wet beta-alumina better than does Na or Na amalgams). Because of this interest, a program is being initiated to study the kinetics of sodium ion exchange across a beta-alumina/organic solvent interface. Several potentially suitable organic solvents are now being investigated. This program will be completed by the end of 1976.

Progress:

The effect of microstructure, and water, on the kinetics of sodium ion diffusion in beta-aluminas has been studied in the temperature range 25°C - 800°C. While grain boundary orientation has a profound effect on the diffusion kinetic, neither grain size nor water have any effect on sodium ion diffusion rate. $^{22}\text{Na}/^{24}\text{Na}$ isotope effect experiments have been studied in the range 25° - 500°C and confirm the results obtained by Yao and Kummer.

A facility for growing single crystal RbAg_4I_5 has been set up.

Degree Recipient:

B. J. Dunbar, Kinetics and Mechanism(s) of Na^+ Transport in Single and Polycrystalline Beta-Alumina.

Papers Presented:

B. J. Dunbar and S. Sarian, "Kinetics and Mechanism(s) of Na^+ Transport in Single and Polycrystalline Beta-Alumina," Pacific Coast Regional Meeting, American Ceramic Society, Seattle, Washington, October 29 - 31, 1975.

W. J. McEntee and S. Sarian, "Effect of Microstructure on the Na^+ Diffusion Kinetics in Polycrystalline Beta-Alumina," Pacific Coast Regional Meeting, American Ceramic Society, Seattle, Washington, October 29 - 31, 1975.

Nuclear Magnetic Resonance (NMR) Ion Mobility Studies

Faculty Supervisor: John L. Bjorkstam, Professor
Electrical Engineering

Graduate Assistant: C. H. Wei, Ph.D. Candidate
Research Assistant

Purpose: To use NMR as a tool for both surveying potentially useful solid electrolytes, as well as for studying the basic mechanisms of ion transport.

Relevance:

a. This research is directed toward achieving a better understanding of the diffusional transport of ions in solids. An ultimate technological goal is improved solid electrolyte batteries.

b. The techniques developed will be applicable to atomic motion studies in other materials as well as in solid electrolytes. It is part of our long range program of using NMR as a general tool for studying atomic and molecular motion.

Objectives:

Objectives of the current year are:

1. Improvement of our cw NMR method for measuring diffusion.
2. Comparison of the NMR results on Na^{23} motion in beta-alumina with such motion as determined by other methods.
3. A more complete understanding, and analysis, of the Na^{23} resonance spectrum in hot pressed beta-alumina supplied by Professor Alan Miller.

For the 1976-77 period our objectives will be to compare the motional parameters (i.e., correlation time, activation energy, and diffusion constant) for ions in selected superionic conductors, as obtained from NMR, with those obtained using other techniques. In particular we wish to compare internal consistency of the three NMR methods (direct diffusion measurement, line narrowing vs. temperature, T_1 minimum vs. temperature), as well as to compare the NMR results with those of tracer, and extended x-ray absorption fine structure (EXAFS) techniques. A second objective is to use the Na^{23} resonance spectrum to quantify the fraction of (grain boundary/crystallite) composition of hot pressed beta-alumina.

Progress:

A major accomplishment during this period has been discovery of a new modulation scheme which we believe will make our cw method for measuring

diffusion at least equivalent in sensitivity to pulse methods. As mentioned in the report of June 1975, while we understood the reason for problems in our method as previously developed, no solution seemed theoretically tractable. The previous analysis was for a sinusoidally varying magnetic-field-gradient (MFG) modulation. Working together with Dr. Janez Stepisnik (a previous post doctoral student on the grant -- now at the University of Ljubljana, Yugoslavia), we have been able to carry out the analysis for MFG modulation of successive, opposite polarity, rectangular pulses of arbitrary duration. A paper is in preparation which fully describes the technique. We will soon be carrying out confirming experiments.

Despite improvements in the cw method for directly measuring the diffusion constant, the possibility of making such a measurement on Na^{23} in beta-alumina seems remote. It has been confirmed that our initial experiments, indicating a short spin-lattice relaxation-time of $T_1 \approx 1$ msec at room temperature and 14 Mhz (there was a typographical error giving $T_1 \approx 1$ sec in the June 1975 report), are indeed correct. In fact, at the T_1 minimum, the value is even shorter. Such a short T_1 will make implementation of direct diffusion measurements by NMR extremely difficult, if not impossible, in this material.

Fortunately we have made considerable progress on another NMR method which allows determination of the Na^{23} motional parameters in beta-alumina. We have been able to extend measurements on the Na^{23} line narrowing in single crystals to temperatures below the knee of the linewidth vs. temperature curve. This knee is at $T \approx 100^\circ\text{K}$, $\tau = 3(10^{-5})$ sec. Analysis of the temperature dependence is in progress. If the activation energy so determined is in agreement with conventional diffusion measurements, the proportionality factor between τ and the diffusion constant will be known. This is an important piece of data to provide a check on theoretical models for diffusion in this material.

Papers Presented:

C. H. Wei and J. L. Bjorkstam, " Na^{23} Nuclear-Magnetic-Resonance Studies in Single Crystal and Hot-Pressed Beta-Alumina," Pacific Coast Regional Meeting, American Ceramic Society, Seattle, Washington, October 29 - 31, 1975.

Grain Boundary Effects in Beta-Alumina

Faculty Supervisor: Alan D. Miller, Assistant Professor
Ceramic Engineering

Graduate Assistant: Douglas O. Powell, Ph.D. Candidate
Research Assistant

Purpose: The purpose of this project is to improve the understanding of the role of grain boundaries in the conduction process in fast ionic conductors, particularly in beta-alumina. The effects of grain boundaries will be studied with respect to their purity, orientation and extent.

Relevance:

Since the application of solid electrolytes will almost certainly involve polycrystals rather than single crystals, it is important to understand the degree of influence of grain boundaries upon the conduction process. Any contribution as to the nature of the conduction process will help to provide a predictive capability in the development of improved systems. If the results can be generalized to describe the importance of boundary processes in low-activation energy electrolytes, a further predictive capability will be realized. This work, which utilizes a.c. conductivity measurements as an experimental tool, is complementary to the tracer diffusion studies on polycrystalline beta-alumina being done under Professor Sarian's supervision.

Objectives:

Objectives for 1975-76 are:

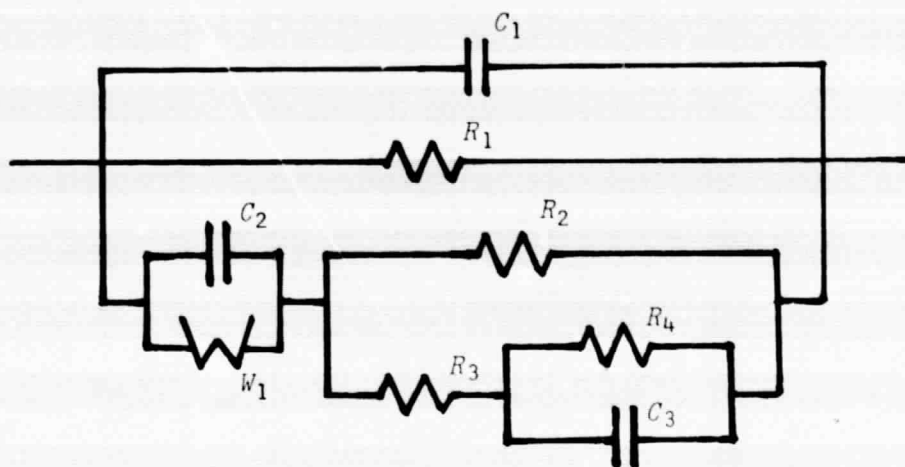
1. To evaluate the a.c. conduction behavior of oriented polycrystalline specimens by comparison with the behavior of equivalent circuit models of possible processes occurring in the specimen.
2. To correlate the results of the a.c. conduction experiments with results from tracer diffusion experiments on polycrystalline specimens.
3. To verify the applicability of chosen equivalent circuit models by varying sample geometry and by conducting four-probe measurements.

Objectives for 1976-77 are:

1. Collect and analyze data on a relatively large number of specimens of varying microstructure, geometry and electrode configurations.
2. In conjunction with Dr. Sarian, to develop a physical model of the grain boundary region in beta-alumina which will improve our ability to predict microstructural effects upon d.c. conductivity.

Progress:

During this report period, analysis of the a.c. conduction behavior of hot-pressed sodium beta-alumina, with respect to the equivalent circuit model presented in the previous report, was continued. Analysis was limited to samples employing fired-on gold electrodes since the a.c. conduction behavior is much simpler than that of the specimens with sodium aluminum ferrite electrodes. The model as presented in the last report is shown below.



where C_1 = capacitance for ideal dielectric between electrodes

C_2 = space charge capacitance at electrodes

C_3 = space charge capacitance at grain boundaries

R_1 = leakage resistance, e.g., surface conduction

R_2 = continuous grain boundary path resistance

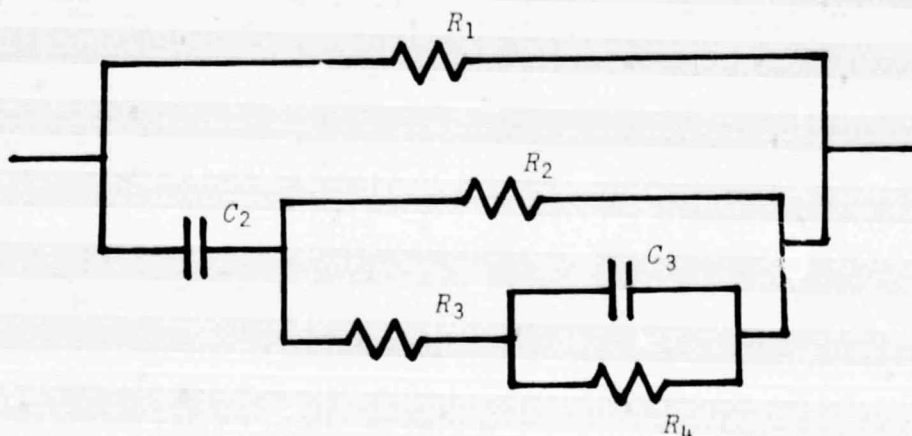
R_3 = resistance to fast-plane conduction within crystallites

R_4 = resistance to cross boundary conduction

W_1 = Warburg impedance due to Faradaic processes at the electrode which only occurs if applied voltage is greater than the discharge voltage of the sodium ions at the electrodes.

For reasonable values of C_1 , calculations have shown that it has a negligible effect on the admittance behavior of the circuit and can

therefore be neglected. For small applied voltages W_1 may likewise be neglected. With these simplifications the model becomes:



By assuming that R_2 is very much greater than R_3 and R_4 , it is possible to determine values for R_1 , R_3 and R_4 from the intercepts of a complex admittance plot with the real axis. The assumption of large R_2 is reasonable since physically R_2 arises from small cross-section, long conduction path processes in a medium (the grain boundary) of relatively high resistivity.

The variation of R_3 and R_4 with temperature allows calculation of activation energies for in-plane and cross-boundary conduction, respectively. These activation energies have been calculated from our experimental data and yield the following values:

In-plane conduction	3.9 kcal/mole
Cross-boundary conduction	9 - 10 kcal/mole

The in-plane value is in excellent agreement with accepted values for single crystal specimens. The cross-boundary value appears to be 2 - 3 kcal/mole high when compared to the tracer diffusion values obtained by Dr. Sarian and co-workers.

Our present work involves constructing a new measurement fixture to be coupled with a more precise and flexible instrument for measuring the specimen impedance. The new instrument will extend our frequency range from 6.3 hz - 400 khz to 0.1 hz - 13 Mhz. The new fixturing provides a well-defined specimen lead configuration which will allow better corrections for stray lead capacitance and conductance. We are also in the process of designing a system using the four-probe technique which may give much better data by avoiding the effects of the electrode double layer capacitance.

Near term measurements will be made on specimens of varying geometry to verify the assignment of various circuit parameters to physical processes in the specimen. For example, if C_2 is indeed the electrode double layer capacitance, then C_2 will be proportional to the electrode area and unaffected by the distance between electrodes. Similarly, R_3 and R_4 will be proportional to the sample length divided by the sample area.

Papers Presented:

D. O. Powell and A. D. Miller, "A Model for Conduction in Polycrystalline Beta-Alumina," Pacific Coast Regional Meeting, American Ceramic Society, Seattle, Washington, October 29 - 31, 1975.

Study of Solid Electrolyte Ceramics Using EXAFS

Faculty Supervisor: E. A. Stern
Professor, Physics

Purpose: To probe the atomic environment surrounding the conducting ions to obtain details and understanding of the conduction process. The suitability of EXAFS to accomplish this will be evaluated -- EXAFS standing for extended x-ray absorption fine structure can ideally determine the location and types of surrounding atoms and the valence state of the ion.

Relevance:

An understanding of the basic mechanism that leads to high ionic conductivity will, hopefully, guide the development of materials suitable for high density power sources. By determining the atomic environment around the active ion as a function of its conductivity, the contribution of local atomic structural environment and electronic state of the ion to the conductivity can be determined by EXAFS. This is required basic information to understand ionic conduction.

Objectives:

To measure EXAFS in RbAg_4I_5 where the environments around every constituent separately can be determined. To determine in practice how much of the ideal information can be obtained.

Progress:

The Stanford Synchrotron Radiation Project storage ring was shut down over the summer and, when it started operating in October, it operated at a low energy where insufficient intensity of the required high energy x-rays was available to make the required measurements.

Paper Presented:

E. A. Stern, "The Investigation of Superionic Conductors by a New Method, EXAFS," Pacific Coast Regional Meeting, American Ceramic Society, Seattle, Washington, October 29 - 31, 1975.

CERAMIC FIBER RESEARCH AREA

Professor David B. Fischbach, Area Coordinator

Relevance:

The utilization of ceramic fibers, including carbon fibers, as engineering materials has increased at a staggering rate over the past decade. Ultimate use of their capabilities as thermal insulation and as a high modulus reinforcing material in metal, polymer, or ceramic matrices has been limited by a lack of sufficient basic knowledge of the fibers themselves and of the interactions between the fibers and their environment.

Goals:

1. To extend the existing knowledge of the fundamental nature of ceramic fibers as related to composition, structure, and surfaces and the effect on properties.
2. Develop knowledge upon which fibers can be produced having appropriate properties.
3. Gain an understanding of the interactions of fibers with their immediate environment and the relations of these to bulk properties of fiber-containing materials.

Mechanical Behavior of Carbon Fibers

Faculty Supervisor: David B. Fischbach, Research Associate Professor
Ceramic Engineering

Graduate Assistants: Roy E. Henrichsen, Ph.D. Candidate
Research Assistant

Seshadri Srinivasagopalan, Ph.D. Student
Research Assistant

Purpose: To investigate the dynamic (and static) stress-induced behavior of carbon fibers and its relationship to structure and processing history.

Relevance:

Mechanical properties are important in most carbon materials applications. The dynamic elastic modulus and damping characteristics of carbons are being investigated to gain new insights into the relationship of mechanical behavior to microstructure. The studies are directed toward carbon fibers for several reasons: Fibers are available in a wide range of microstructural types, representing all of the major precursor/processing categories of synthetic carbon materials (i.e., polymeric, mesophase and CVD); microstructural characteristics and structural development behavior of several carbon fiber types have been the subjects of extensive study both there and elsewhere; fibers have great applications importance, primarily in composite materials. A torsion pendulum technique is being used because it is ideally suited to fibrous forms; and the method is straightforward and versatile, permitting dynamic measurements under static stress. Furthermore, the pendulum results are weighted in favor of the near-surface properties, which are especially important in composite fiber/matrix interactions; and little information is available on the torsional behavior of carbon fibers.

Some work has also been done on the microhardness characteristics of some homogeneous bulk carbon materials (glassy and pyrolytic carbons) to investigate the nature of the indentation processes and the usefulness of this technique for carbon material characterization and study of mechanical behavior.

Goal:

All aspects of the carbon materials research here have a common goal: A useful and effective materials science of carbons based on understanding of structure, its origins and development, and its relationship to properties. A sub-goal for this project is understanding of the mechanical behavior of carbon materials.

Objectives:

1. Determine the torsional modulus and damping characteristics and investigate nonlinear elastic behavior of representative commercial carbon fiber types at room temperature.
2. Relate the observed stress-induced behavior to the structure and processing history of the fibers.
3. Extend these studies to new fiber types (e.g., anisotropic pitch mesophase; CVD).
4. Investigate the temperature-dependence of the stress-induced behavior.

Progress:

During this reporting period, work has progressed along the lines projected in the previous status report. Henrichsen completed the rough draft of his Ph.D. thesis which provides an exceptionally thorough account of the experimental techniques developed and the results obtained on as-received commercial fibers. The torsion pendulum apparatus has been reassembled and adjusted after repair and modification of the vibration isolation base, and fiber mounting techniques have been modified to increase the success rate. Methods to improve the measurement accuracy of the pendulum period and the fiber cross sectional dimensions were explored. Data obtained on additional as-received rayon- and PAN-based fiber types are in agreement with earlier results on comparable fibers. In an effort to identify and reduce sources of background damping, the air damping contribution was redetermined using a silica fiber. At the normal operating vacuum of about 10^{-5} torr, the log decrement contribution from residual air damping was found to be approximately 3×10^{-6} , two orders of magnitude less than the smallest fiber damping values that have been observed. If there is any significant apparatus background contribution to the measured fiber damping values, it must come from other sources -- most probably the glue joints attaching the fiber to the end supports and to the mirror inertial bob. Techniques to evaluate this damping source are under consideration. Procurement of anisotropic pitch fibers from two sources was initiated. Attempts to observe piezoresistive effects in carbon fibers by using available equipment were unsuccessful, and further work on that problem has been suspended pending the outcome of a proposal now under consideration by the Army Research Office that would provide additional equipment and research assistant support.

Additional observations on the microhardness indentation behavior of glassy carbons, as-deposited and well graphitized pyrolytic carbons further demonstrated both the difficulty and the great importance of obtaining adequate image definition for the correct measurement of

indent sizes on carbon materials. Using a variety of techniques (SEM, optical polarized light and interference contrast microscopy on surfaces coated with various thicknesses of evaporated metal coating applied before or after indentation), several errors and ambiguities in previous results were removed. A paper was presented on the results.

During the next six months it is planned to continue efforts to improve the dynamic measurement techniques, initiate studies on the influence of laboratory heat treatments on the stress-induced behavior of selected commercial fiber types; and begin investigation of the dynamic mechanical characteristics of new fiber types.

Papers Presented:

D. B. Fischbach, "Fibers of Carbon, 2000 A.D.: Some Notes for an Extrapolation from the Present Status," Pacific Coast Regional Meeting, American Ceramic Society, Seattle, Washington, October 29 - 31, 1975.

Seshadri Srinivasagopalan and D. B. Fischbach, "Microhardness of Pyrolytic Carbon and Graphite," Pacific Coast Regional Meeting, American Ceramic Society, Seattle, Washington, October 29 - 31, 1975.

Papers Published:

R. E. Henrichsen and D. B. Fischbach, "Torsional Nonlinear Elasticity and Damping of Carbon Fibers," Extended Abstracts and Program, Twelfth Biennial Conference on Carbon, University of Pittsburgh, July 28 - August 1, 1975. pp. 135-6.

Kinetics and Mechanisms of Graphitization

Faculty Supervisor: David B. Fischbach, Research Associate Professor
Ceramic Engineering

Graduate Assistant: Michael E. Rorabaugh, M.S. Candidate

George B. Mellinger, M.S. Candidate

Purpose: To investigate the nature of structural evolution processes in carbons and the influence of microstructural morphology on them.

Relevance:

Under the influence of high temperature heat treatment, the disordered structures of synthetic carbons develop toward the equilibrium crystalline graphite structure via complex thermally activated processes that include the evolution of residual impurities, annealing of structural defects and, perhaps, some structural reorganization. Such thermally-induced graphitization provides the principal method of post-carbonization structural and property development and is of fundamental importance in the processing, technology and understanding of carbon materials. The present focus of this project is on difficult-to-graphitize glassy and fiber (polymeric) carbons in which structural disorder is relatively stable, due apparently to the microstructural morphology. The aim is to gain a better understanding of the processes and limitations involved in structural and property development in these materials.

Goal:

An effective materials science of carbon based on understanding of structure, its development and its influence on properties. A subsidiary goal for the graphitization studies is fundamental understanding of the thermally-induced structural evolution processes.

Objectives:

1. Establish the nature and extent of structural evolution in representative fiber and glassy carbons by determining the effects of isochronal heat treatment in the range 1000 - 3000°C on structure-sensitive characteristics (diamagnetism, density, etc.). (Substantially accomplished for several major types of fiber and glassy carbon).
2. Investigate the kinetic aspects of structural development in these carbons by isothermal heat treatments over selected temperature ranges. (Completed in the 1800 - 2400°C range for several fiber types; data obtained in the 2400 - 3000°C range for glassy carbons.)

Progress:

Data on the effects of isochronal heat treatment on the diamagnetic susceptibility and the density of several glassy carbons (GC) from commercial (Beckwith, Le Carbone, Sigri, Tokai) and laboratory (Battelle Northwest) sources have been obtained over the heat treatment temperature (HTT) range 800 - 3000°C. Data on the influence of isothermal treatment time (HTt) and temperature in the 2400 - 3000°C range have been obtained for several of these carbons. Analysis of the magnetic susceptibility data has been largely completed and a paper was presented on the results.

The isochronal treatments were carried out in argon, heating at 50 C/min. to the HTT, holding for 30 min., then cooling at 50 C/min. Moderate rates are necessary to avoid thermal fracture. Room temperature diamagnetic total (trace) susceptibilities measured at a magnetic field strength of about 0.7 Tesla are plotted against HTT for two representative GCs in Fig. 1. The diamagnetism minimum that develops in the $1000 < \text{HTT} < 1500^\circ\text{C}$ range involves a magnetic field strength dependence of the type usually associated with ferro-magnetic impurities. The dashed curves represent values obtained by extrapolation to infinite field strength; and the slopes of the X vs H^{-1} (Honda-Owen) plots are shown in the inset. No impurities were detected with the EDAX x-ray analysis capability of the SEM, but trace amounts of iron have often been reported in GC spectrographic analyses. The maximum dX/dH value observed (Sigri, 1300°C) corresponds to < 30 ppm by weight of Fe. All of the as-carbonized GC showed evidence of some magnetic impurity, but the amount decreased in the order Sigri, Beckwith, Le Carbone, Battelle. The impurity is evidently present in the GC initially in a para- or diamagnetic form; becomes ferromagnetic due to a change in chemical or aggregation state caused by heat treatment at 1000 - 1300°C; and subsequently disappears for $\text{HTT} \geq 1500^\circ\text{C}$. The detailed mechanisms involved in this process are not understood, but these impurity effects may contribute to peculiarities that have been reported in the low temperature specific heat and other properties of glassy carbons with low HTT. For $\text{HTT} \geq 1700^\circ\text{C}$, the diamagnetic behavior of all of the GC is nearly identical, indicating that electronic structural development is insensitive to material source and precursor. Up to about 2500°C, the principal mechanism other than impurity evolution appears to be annealing of structural defects. X-ray diffraction studies elsewhere have shown that layer distortion decreases and layer perfection increases regularly with heat treatment in this range. Above about 2500°C, the rate of increase of diamagnetism with HTT increases, suggesting that some mechanism of structural reorganization may become operative. After heating to 3000°C the trace susceptibility remains appreciably less than the values for graphites (for perfect graphite $X_T = -22 \times 10^{-6}$ emu/g) but there is still no indication of approach to a limiting value, and it appears that further structural development would result from higher HTT.

Isothermal heat treatments with cumulative durations (HTt) of 5 - 100 min. have been carried out at 100°C intervals over the range 2400 - 3000°C to investigate the kinetics of the structural development processes in

this temperature range. The furnace was heated at a rate of about 100°C/min. with the graphite crucible containing the samples displaced from the central hot zone. After the hot zone temperature was stabilized at the desired HTT, the crucible was pushed into it, resulting in a very rapid heating rate over the final few hundred degrees of temperature rise. This procedure permitted good definition of the isothermal HTt with a low incidence of thermal fracture (the carbon exhibits some plasticity above about 2000°C). Curve superposition analysis of the data shows that the effective activation energy is very high, 350 - 400 kcal/mole, in general agreement with earlier results on the high temperature structural development of difficult-to-graphitize fluidized bed pyrocarbons, and the tensile creep behavior of glassy carbon. These energies are too high to be explained by normal defect diffusion mechanisms; they suggest that structural rearrangement processes involving the simultaneous or sequential rupture of many carbon-carbon bonds may be rate determining.

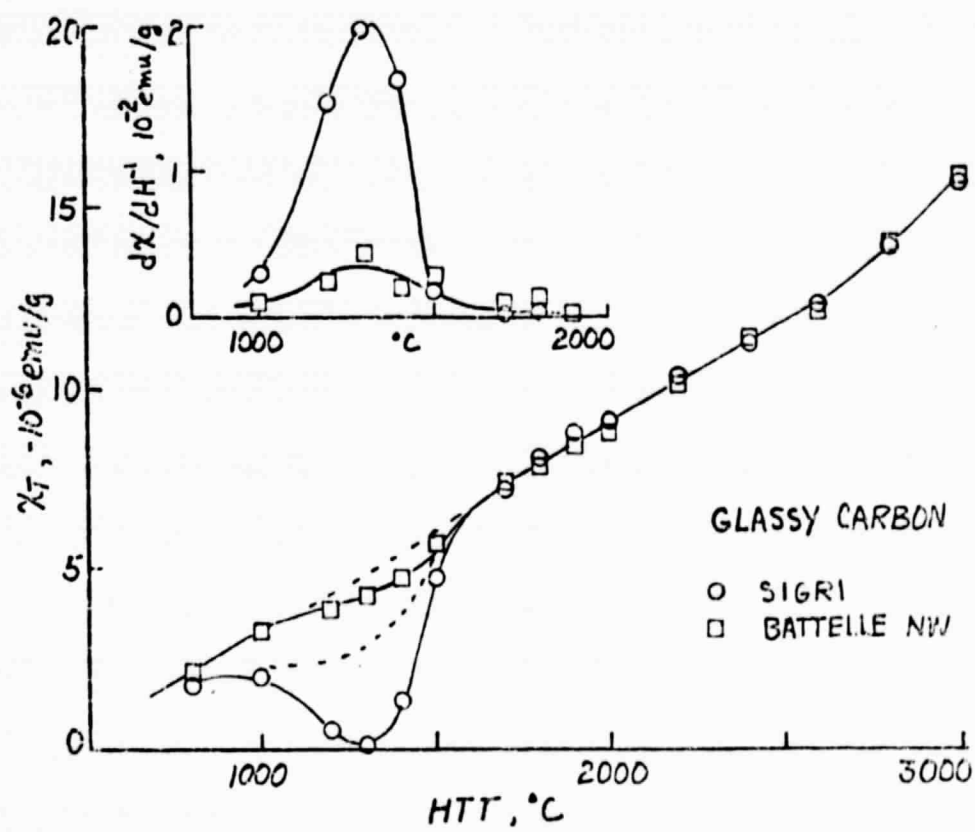
The density of glassy carbon has been found to decrease with increasing HTT, contrary to the behavior of most other carbons. During the next six months, it is planned to complete the analysis and evaluation of data on density changes. Some x-ray diffraction data on carbon fibers have been obtained and are being analyzed.

Paper Presented:

M. E. Rorabaugh and D. B. Fischbach, "Glassy Carbon 'Graphitization'," Pacific Coast Regional Meeting, American Ceramic Society, Seattle, Wa., October 29-31, 1975.

Paper Published:

G. B. Mellinger and D. B. Fischbach, "Diamagnetic Studies on Carbon Fiber Graphitization," Extended Abstracts and Program, Twelfth Biennial Conference on Carbon, University of Pittsburgh, July 28 - August 1, 1975, pp. 277-8.



Laser Raman Spectroscopy of Carbon Materials

Faculty Supervisors: David B. Fischbach, Research Associate Professor
Ceramic Engineering

John W. Macklin, Assistant Professor
Chemistry

Graduate Assistant: Ron Vidano, Ph.D. Student
Research Assistant

Purpose: To investigate the nature of the Raman activity of disordered carbons and defective graphites, and to assess its utility as a structural characterization technique.

Relevance:

Properties and behavior of carbon materials are especially structure-dependent, and a wide range of structural morphology and imperfection results from the great variety of precursors and processing methods used in their manufacture. The very disordered structures characteristic of carbons are difficult to characterize unambiguously, and there is a need for effective new techniques to supplement diffraction and microscopy methods. Surface and interface structures are especially important in applications areas such as composites (fiber/matrix interactions) and friction and wear. An exploratory investigation here has demonstrated that Raman spectroscopy has real promise as a method for carbon material characterization, and for surface structure studies. It is felt that new basic knowledge about structural imperfection in carbons may be obtained from a better understanding of the Raman activity of these materials.

Goal:

This project shares a common goal with other carbon materials research in progress here: Development of a true materials science of carbon based on understanding of structure and its influence on properties.

Objectives (revised):

1. Determine the spectral characteristics of several varieties of carbon as a function of type and treatment to assess the usefulness of this technique for the characterization of both virgin and treated surface structures and textures.
2. Investigate the origins and nature of the Raman spectral characteristics, especially the line associated with structural disorder, and their relationship to structural morphology and defects.

Progress:

During this reporting period a new graduate assistant was initiated into the project. An improved sample holder was developed and various arrangements for excitation and collection of Raman radiation were evaluated. A modification of the 180° scattering technique was developed which gives improved performance for many carbon sample types. The mirror that reflects the exciting beam onto the sample was moved off the spectrometer optical axis so that the collecting lens aperture is not obscured, but a high angle of incidence is maintained and Raman radiation emitted normal to the surface is collected. Additional data on glassy carbons (GC), fluidized bed (FBPC) and massive (MPC) pyrolytic carbons were obtained and analyzed. The usefulness of the W_G (graphite line width) vs R_i (intensity ratio, I_D/I_G) plot for material characterization was confirmed and extended. However, some details of the plot published in the previous report may be in error. New spectra on GCs heat treated below 1800°C have not confirmed the peak in W_G , but suggest a maximum in R_i instead. Some FBPCs have very large line widths, $> 100\text{ cm}^{-1}$; whereas low deposition temperature MPCs have relatively low line widths, placing them below the other carbon material types in the left (disordered) portion of the diagram. A significant correlation has been observed between diamagnetic susceptibility and Raman R_i value, with generally different characteristics for GC, MPC and FBPC. An inverse relationship between R_i and apparent layer diameter L_a , reported in the literature, was confirmed. However, it also appears to depend on carbon type (for the same L_a value, R_i of MPCs is much greater than that of GCs). A difference was anticipated since L_a has the significance of a mean defect-free distance, and its value might be expected to depend on structural morphology and the nature of the defects. However, the direction of the result is contrary to expectations and the interpretation is not yet clear. During the next six months, it is planned to initiate a survey of the Raman characteristics of carbon fibers; to extend previous studies on the effects of surface treatment on the spectra of various carbon types; to resume investigation of the anisotropy of the Raman response of PC and compression-annealed PC; and to determine the Raman spectrum of BN which has a hexagonal layer structure analogous to that of graphite. The primary objective of the latter studies is a better understanding of the origin(s) of the disorder line.

Paper Published:

T. G. Miller and D. B. Fischbach, "Structural Characterization of Carbon Materials by Laser Raman Spectroscopy," Abstracts of Papers and Program, Twelfth Biennial Conference on Carbon, University of Pittsburgh, 28 July - 1 August 1975, pp. 105-6.

Pore Characteristics of Silica Fibers

(Supported by the NASA-Ames University Consortium.)

Faculty Supervisor: O. J. Whittemore, Jr., Professor
Ceramic Engineering

Graduate Assistant: Anil Jain, M.S. Candidate
Research Assistant

Purpose: To obtain knowledge regarding the nature of the porosity and the effects upon sintering of microporous silica fibers.

Relevance:

The use of leached silica fibers for reusable surface insulation on the space shuttle, based not only upon the refractory and insulative properties but also upon the stability of the material. This work will aid in the processing and give insight into fiber stability in use.

Objective:

Study the pore size distribution of microporous silica fibers (initial pore diameters of about 4 nm) after sintering at various times and temperatures to develop a model for pore removal by viscous flow shrinkage.

Progress:

Previous studies have shown the mean pore diameter to increase with sintering. However, since the pressure acting due to surface tension is inversely proportional to pore diameter, small pores would shrink first thus explaining a mean pore growth. It is hoped to prove this hypothesis.

Surface area measurements have been made on several fiber samples received to date. Some of these samples had very low surface areas ($220 \text{ m}^2/\text{g}$) and others showed a wide range of surface area (20 to $130 \text{ m}^2/\text{g}$) in several specimens from individual samples. A means of obtaining sample homogeneity has been developed which, in at least one sample (21 HP), appears to have eliminated this problem. Measurements on several "as-received" specimens resulted in surface areas of from 70 to $100 \text{ m}^2/\text{g}$. After homogenization, the measurements ranged from 120 to $130 \text{ m}^2/\text{g}$.

A method was developed to get the pore size distribution of the fibers using sorBET which is actually used for determining surface area only.

While determining pore size distribution, surface areas as well as pore volume can be determined, thus giving all the required information. Pore volumes of some samples were determined by using carbon tetrachloride and n-hexadecane solution.

Optical Waveguides and the Strength of Optical Glass Fibers

(Supported by the Naval Electronics Laboratory Center, San Diego, California.)

Faculty Supervisor: William D. Scott, Associate Professor
Ceramic Engineering

Research Faculty: G. Achutaramayya, Research Associate
Ceramic Engineering

Purpose: The purpose of this work is to develop special shaped waveguide structures for coupling sources to optical fibers and to evaluate the strength of long lengths of optical fibers.

Relevance:

The rapidly developing technology of optical communications requires improvements in coupling and fiber reliability.

Progress:

This is a cooperative research program in which design parameters furnished by the Department of Electrical Engineering are used as the basis for fabricating glass fibers and unusual shaped optical waveguides. These special shapes included rectangular ribbon guides exposed on supporting substrates or totally enclosed with overall cross-sections of 50 by 400 μm and guiding regions from $1 \times 25 \mu\text{m}$ to $10 \times 200 \mu\text{m}$. These configurations are currently being used in experiments on coupling light from planar components and from rectangular injection laser sources into round optical fibers. Transition structures have now been fabricated from glasses other than Pyrex-type in order to achieve better index matching with proposed sources.

A statistical analysis of the strength of polymer coated silica fibers has been completed by listing 120 samples from four drawing runs with test gage length of 70 cm. Weibel analysis indicates minimum strengths of about 60.9 MN/m² (10,000 psi) for kilometer long lengths.

A proposal to continue the investigation of high-strength coated fibers is pending with the U.S. Army Research Office, and proposals for continuing the work on transition structures have submitted to the National Science Foundation and the Naval Electronics Laboratory Center.

Paper Presented:

W. D. Scott and G. Achutaramayya, "Fabrication and Strength of Glass Fiber Waveguides," Pacific Coast Regional Meeting, American Ceramic Society, Seattle, Washington, October 29 - 31, 1975.

Paper Published:

David G. Dalgoutte, Gordon L. Mitchell, Robert L. K. Matsumoto, and William D. Scott, "Transition Waveguides for Coupling Fibers to Semiconductor Lasers," Applied Physics Letters, 27(3), 125-6, 1975.

Faculty Supervisor: William D. Scott, Associate Professor
Ceramic Engineering

Graduate Assistants: Keunho Orr, Ph.D. Candidate
Research Assistant

K. Komaki, Ph.D. Student
Research Assistant

Purpose: The purpose of this work is to define the conditions of stress, temperature and surface characteristics which influence the formation and growth of deformation twins in aluminum oxide.

Relevance:

Twinning is an important mode of deformation in aluminum oxide. Single crystals of this material are used in laser rods, laser windows, high intensity arc lamp windows and envelope tubes and as substrates for epitaxial growth of silicon. The presence of twins in these components is detrimental to their successful use.

Twin-twin and twin-grain boundary interactions are known to cause fractures in alumina single crystals. We have shown that rhombohedral twins can be formed in alumina in the stress range 4 MN/m² (580 psi) to 25 MN/m² (3640 psi) in the temperature range 500 to 1100°C. There are low stresses and low deformation temperatures for alumina. Understanding of these deformation processes will help improve the mechanical properties of alumina, the most widely used ceramic oxide.

Objectives:

1. First year - completed. To obtain twinning in oriented compression specimens and to determine approximate stress - temperature characteristics.
2. Second year - in progress - present work. To measure systematically the temperature dependence and stress dependence of twinning and to extend the measurements to lower temperatures than previously investigated.
3. Third year. To examine the details of twin growth and the influence of surface condition on twin formation and crack initiation.

Progress:

Work has continued on the temperature and strain rate dependence of yield drop during twinning. At the lowest strain rate (10^{-6} sec⁻¹) the transition temperature for yield drop was 600 to 650°C, i.e., at 600°C and

below, no yield drop, at 650° slow yield drop. These results were for as-received ground surface specimens. When similar crystals were annealed at 1450°C for 6 hours before the compression test, a yield drop occurred at 600°C. Comparison of polished and ground surfaces did not show any difference in yield behavior, but, in general, specimens with polished surfaces twinned at a lower stress.

Compression tests were carried out at temperatures below 500°C with the following results:

400°C	Twinning	30 - 35	MN/m ²
350°C	Twinning	45 - 50	MN/m ²
300°C	Fracture	250 - 300	MN/m ²
25°C	Fracture	" "	

Thus, 350°C was the lowest temperature at which large-scale twinning has been observed. At 300°C and 25°C fracture occurred at relatively low stresses compared to the normal compressive strength of polycrystalline alumina (~ 3450 MN/m²). The fractures were unusual in that the crystals were split along the axis of the cylindrical specimen. This behavior may be caused by end effects, and this is being investigated further using a new three-dimensional stress analysis program recently developed by Mr. G. Das who is completing his Ph.D. thesis.

Mr. Kunio Komaki joined the program in September and has been attempting to nucleate twins on hardness indentations. This has been unsuccessful to date.

Paper Presented:

W. D. Scott, "Twinning in Sapphire Crystals," Pacific Coast Regional Meeting, American Ceramic Society, Seattle, Wa., October 29-31, 1975.

This work is now supported by the National Science Foundation.

CERAMIC PROCESSING

Professor O. J. Whittemore, Jr., Area Coordinator

Relevance:

The manufacture of products from ceramic materials includes the use of high temperatures to develop the appropriate properties of the product. The study of pre-shrinkage sintering has been generally overlooked, yet subsequent grain-growth appears to be highly dependent upon these initial stages. Knowledge of this would be relevant to any NASA utilization of sintered ceramics, and possibly metals.

Goals:

To obtain knowledge of the effects of surface properties of ceramic materials upon the mechanisms involved in the initial pre-shrinkage stages of sintering.

Ceramic Processing - Sintering

Faculty Supervisor: O. J. Whittemore, Jr., Professor
Ceramic Engineering

Graduate Assistant: Kunio Aihara, Ph.D. Candidate
Research Assistant

Purpose: To study the initial stage of sintering of magnesium oxide, particularly where pore growth occurs.

Relevance:

Of the various stages in the processing of manufacture of ceramics, sintering most determines the final microstructure. The initial stage of sintering includes reduction of surface, formation of necks between particles, and, in some cases, coalescence of a fraction of the particles. Densification and shrinkage may not occur so if surface is reduced, pores must be growing. The sintering of ceramics showing this behavior is the object of this work. This research thus develops knowledge useful in the manufacture of ceramics. One result may be the recognition of an optimum initial particle size and shape for sintering to maximum density with minimum grain size rather than a minimum initial size as has usually been advocated. Another result may be better understanding of the manufacture of catalysts, catalyst supports, filters, adsorbents and other porous high-surface ceramics. The knowledge developed has been applied to studies of carbon composites, animal bone, and to studies of the sintering of the raw material for reusable space insulation, microporous silica fiber.

Objectives:

1. Study the initial stage of sintering magnesia, particularly the effects of morphology and sintering atmosphere on pore growth and densification.
2. Preparing a joint proposal with Professor Halsey for future work on other materials. (1975 for work beginning in 1976.)

Progress:

Initial stage of sintering of MgO has been studied choosing sub-micron size particles as a starting material. Two kinds of MgO were prepared, one by calcination of $\text{Mg}(\text{OH})_2$ and the other by burning Mg-metal in oxygen rich atmosphere. Both materials have similar particle size (100 ~ 500 Å) but the difference was (1) MgO smoke showed better cubicity and (2) MgO smoke consists of independent cubes, but MgO prepared from $\text{Mg}(\text{OH})_2$ showed the aggregate of small cubes in original $\text{Mg}(\text{OH})_2$ shape. Sintering behavior of these materials has been studied in different atmospheres.

Previous study indicated that: (1) The firing atmosphere effects on the sintering behavior of magnesia. Water vapor enhances the sintering rate in both shrinkage and in pore growth, but the shrinkage rate is not enhanced as much as the pore growth rate by the water vapor. (2) The kinetic study was done employing the following equations:

$$D^n - D_o^n = k_1 \exp(-Q_1/RT) t \quad \text{for pore growth}$$

and

$$\rho/\rho_o = k_2 \exp(-Q_2/RT) \ln t + C \quad \text{for densification}$$

where: D = pore size at time
 D_o = initial pore size
 ρ = density at time
 ρ_o = theoretical density
 n, C = constant

(3) A SEM study shows the development of (111) plane as sintering progress. This development is greater in water vapor. Employing Wulf's construction method, the surface energy ratios, $\gamma(100)/\gamma(111)$, are obtained for various atmospheres and temperatures.

The following conclusions have been reached. (1) Result (1) denies the sintering mechanism proposed by other investigator; they proposed that grain boundary diffusion is the controlling process in both air and in water vapor but the grain boundary diffusion coefficient is higher in water vapor than in air due to the Mg - vacancy introduced by (OH). (2) Kinetic study employing pore growth or densification equation tells little about the mechanism of sintering but it has value in technological science. These equations tell us which firing condition is adequate to obtain a material of certain pore size and density.

One example of this application is that we made a crucible rid for the surface adsorption study group (Dr. Dash and Dr. Vilches). This rid has to have good N_2 gas permeability and adequate mechanical strength, not too strong to make the machining difficult but strong enough to be handled. To obtain these properties crucible rid were fired at low temperature (1500°C) in water vapor.

(3) Thermodynamical consideration eliminated the possibility of the vapor transport mechanism of MgO in air atmosphere but in water atmosphere vapor pressure of $Mg(OH)_2$ is high enough to give observed growth rate of pores. Possibility of surface diffusion mechanism in water vapor does still exist at this point.

(4) The technique to obtain the energy distribution of adsorption sites on MgO smoke developed by Dr. Hinman and Professor Halsey will be useful to get a morphological information at the initial stage of sintering of sub-micron size particles.

Adsorption on Porous Solids

Faculty Supervisor: G. D. Halsey, Professor
Chemistry

Graduate Assistant: David Hinman, Ph.D. Candidate
Research Assistant

Purpose: To characterize real solid surfaces, as distinguished from idealized lattice surfaces by adsorption studies, and to shed light on the process of sintering.

Relevance:

Real solids are used extensively in industry for the surface properties such as adsorption and catalysis. As yet, there is no satisfactory treatment of the surface heterogeneity of such solids, and one is badly needed.

The author has published a series of papers on this problem over the past twenty-five years, and however reluctantly, physicists and chemists have now come to realize the academic interest as well as practical importance of this difficult problem.

Objective:

Our current objective includes seeking an NSF grant (joint with O. J. Whittemore, Jr.) to support a greater effort in the research area.

Progress:

The project is proceeding on preparing a paper on the argon-tin oxide system based on Hinman's thesis research.

A paper has been written which develops a reasonably simple intuitive model for interaction of a gas with a non-uniform surface that is considerably more realistic than previous theories.

Problem areas include interpretation of tin oxide data, and refinement of experimental apparatus.

Degree Recipient:

David Hinman, Physical Adsorption on Heterogeneous Surfaces MgO and SnO₂.

Papers Presented:

Mr. Hinman presented his work in two seminars in the UW Chemistry Department (September and November) and one in the Ceramic Seminar in December.

Paper Published:

David Hinman and G. D. Halsey, "Adsorption of Argon on a Non-Uniform MgO Surface," Journal of Chemical Physics, to be published.

Surface Characterization; Ceramic Processing

Faculty Supervisors: J. G. Dash, Professor
Physics

O. E. Vilches, Associate Professor
Physics

Graduate Assistant: Manu Tejwani, Ph.D. Candidate
Research Assistant

Purpose: The purpose of this project is to apply refined physisorption measurements to the study of the surface properties of ceramic powders and compacts.

Relevance:

The application of knowledge of the surface characteristics of ceramic powders to ceramic processing should lead to more effective production of many polycrystalline materials currently of interest in many federal programs.

Objectives:

The long range objective of the project is an investigation of sintering in ceramic materials, with particular emphasis on the microscopic surface conditions governing the initial stages. During the forthcoming year we plan to study the quantitative effects of compaction on the speed and extent of sintering well-characterized MgO powder. This work is an extension of the findings of the current year's research, i.e., that the surface homogeneity of MgO cube crystal powder is degraded by compaction. Here we distinguish between relatively mechanical aspects of compaction, i.e., the increase of contact area, and the crystallographic changes due to microscopic fractures and strains. We believe that this has important implications for the sinterability of uniform powders and perhaps of the ease of sintering typical heterogeneous materials.

The techniques used in this study involve the physical adsorption of simple gases. Various adsorption characteristics, such as vapor pressure isotherms, and indicators of the microscopic and macroscopic states of surfaces: total surface area, binding energy, and uniformity. We use the vapor pressure of Kr for the MgO study, to evaluate the several procedures used in preparing samples and improving their homogeneity. In addition we expect to develop ancillary diagnostic methods in collaboration with other groups: these include nuclear magnetic resonance and neutron diffraction of the bare and film-covered samples, both before and after compaction and sintering. Within the CMR complex there are capabilities for determining the degree of sintering by means of mechanical measurements such as crushing strength, and these techniques will be utilized in collaboration with other faculty supervisors.

Progress:

The past six months have seen considerable progress in preparation of high uniformity samples. A small quantity of MgO smoke was studied by Kr adsorption after successive heat treatments in vacuum at progressively higher temperatures. Isotherms improved in several features until after treatment at 900°C they displayed a particularly characteristic feature which has been seen previously only in a small number of highly uniform adsorption systems, a vertical riser indicating a region of phase coexistence between a gaseous and a liquid film phase. This feature persisted even after the sample was exposed to air and then reheated at moderate temperature, thus indicating that the surface uniformity is quite stable and reproducible in the course of moderate or casual storage. We have loaned this small sample to a former colleague at Wesleyan University, who will use it as substrate for a study of adsorbed He^3 by nuclear magnetic resonance.

We have developed a modified technique which will be used to prepare larger quantities of MgO smoke, larger quantities being necessary to the next stages of the study.

APPENDIX I

Ceramic Materials Research Committee

Associate Dean H. M. Swarm, Chairman - representing the Dean of the College of Engineering.

Professor E. C. Lingafelter, Department of Chemistry - representing the Office of University Research.

Professor J. G. Dash, Department of Physics - representing the Dean of the College of Arts and Sciences.

Professor J. I. Mueller, Ceramic Engineering Division - Principal Investigator, NASA Grant.

Professor D. G. Dow, Department of Electrical Engineering.

Professor T. G. Stoebe, Metallurgical Engineering Division.

Professor W. D. Scott, Ceramic Engineering Division.

APPENDIX II.

List of Papers Presented:

B. J. Dunbar and S. Sarian, "Kinetics and Mechanism(s) of Na^+ Transport in Single and Polycrystalline Beta-Alumina," Pacific Coast Regional Meeting, American Ceramic Society, Seattle, Washington, October 29 - 31, 1975.

D. B. Fischbach, "Fibers of Carbon, 2000 A.D.: Some Notes for an Extrapolation from the Present Status," Pacific Coast Regional Meeting, American Ceramic Society, Seattle, Washington, October 29 - 31, 1975.

W. J. McEntee and S. Sarian, "Effect of Microstructure on the Na^+ Diffusion Kinetics in Polycrystalline Beta-Alumina," Pacific Coast Regional Meeting, American Ceramic Society, Seattle, Washington, October 29 - 31, 1975.

D. O. Powell and A. D. Miller, "A Model for Conduction in Polycrystalline Beta-Alumina," Pacific Coast Regional Meeting, American Ceramic Society, Seattle, Washington, October 29 - 31, 1975.

M. Rorabaugh and D. B. Fischbach, "Glassy Carbon 'Graphitization'," Pacific Coast Regional Meeting, American Ceramic Society, Seattle, Washington, October 29 - 31, 1975.

W. D. Scott and G. Achutaramayya, "Fabrication and Strength of Glass Fiber Waveguides," Pacific Coast Regional Meeting, American Ceramic Society, Seattle, Washington, October 29 - 31, 1975.

W. D. Scott, "Twinning in Sapphire Crystals," Pacific Coast Regional Meeting, American Ceramic Society, Seattle, Washington, October 29 - 31, 1975.

Seshadri Srinivasagopalan and D. B. Fischbach, "Microhardness of Pyrolytic Carbon and Graphite," Pacific Coast Regional Meeting, American Ceramic Society, Seattle, Washington, October 29 - 31, 1975.

E. A. Stern, "The Investigation of Superionic Conductors by a New Method, EXAFS," Pacific Coast Regional Meeting, American Ceramic Society, Seattle, Washington, October 29 - 31, 1975.

C. H. Wei and J. L. Bjorkstam, " Na^{23} Nuclear-Magnetic-Resonance Studies in Single Crystal and Hot-Pressed Beta-Alumina," Pacific Coast Regional Meeting, American Ceramic Society, Seattle, Washington, October 29 - 31, 1975.

List of Papers Published:

David G. Galgoutte, Gordon L. Mitchell, Robert L. K. Matsumoto, and William D. Scott, "Transition Waveguides for Coupling Fibers to Semiconductor Lasers," Applied Physics Letters, 27(3), 1975, pp. 125-6.

R. E. Henrichsen and D. B. Fischbach, "Torsional Nonlinear Elasticity and Damping of Carbon Fibers," Extended Abstracts and Program, Twelfth Biennial Conference on Carbon, University of Pittsburgh, July 28 - August 1, 1975, pp. 135-6.

David Hinman and G. B. Halsey, "Adsorption of Argon on a Non-Uniform MgO Surface," Journal of Chemical Physics, to be published.

G. B. Mellinger and D. B. Fischbach, "Diamagnetic Studies on Carbon Fiber Graphitization," Extended Abstracts and Program, Twelfth Biennial Conference on Carbon, University of Pittsburgh, July 28 - August 1, 1975, pp. 277-8.

T. B. Miller and D. B. Fischbach, "Structural Characterization of Carbon Materials by Laser Raman Spectroscopy," Abstracts of Papers and Program, Twelfth Biennial Conference on Carbon, University of Pittsburgh, July 28 - August 1, 1975, pp. 105-6.

Theses:

B. J. Dunbar, Kinetics and Mechanism(s) of Na⁺ Transport in Single and Polycrystalline Beta-Alumina, M.S. Thesis, 1975.

David Hinman, Physical Adsorption on Heterogeneous Surfaces MgO and SnO₂, Ph.D. Thesis, 1975.